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SHORT COMMUNICATION

A high productivity and speedy synthesis process for copper nanowires via an ethylenediamine-mediated method

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Abstract Generally, there are two well-known synthetic approaches for copper nanowires (Cu NWs): ethylenediamine (EDA)-mediated synthesis and alkylamine-mediated synthesis. The alkylamine-mediated synthesis produces very high ratio nanowires but requires a special environment and long reaction times, while the EDA-mediated synthesis can be carried out under normal conditions and requires from 30 min to 1 h. However, the Cu NWs produced by this method have an average aspect ratio lower than 500 and are produced in low yield. In this paper, we present a modified EDA-mediated synthesis to improve the yield and reduce the synthesis time. In previous reported EDA-mediated synthesis, sodium hydroxide (NaOH) was used as a pH adjusting element and the reaction was performed at high temperature. By replacing NaOH with potassium hydroxide (KOH) and cooling down the temperature of reaction to room temperature, the synthesis time was reduced to 15 min as well as the productivity of high aspect ratio Cu NWs was increased notably to 80%. Furthermore, the transparent electrodes which were fabricated based on the as-synthesized Cu NWs, exhibited high performance, such as 23.5 Ω/sq of sheet resistance and 81% of transmittance at $\lambda = 550$ nm.

Keywords Nanomaterials synthesis · Productivity · Copper nanowires · Ethylenediamine · Transparent electrode

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Introduction

Currently, indium tin oxide (ITO) is the dominant transparent conductor material in various optoelectronic devices such as organic light emitting diodes (OLEDs), flexible solar cells, and touch-screens. The high transmittance (>90%) of ITO at low sheet resistances (10 Ω/sq on glass) is the primary reason for its popularity. However, ITO has several undesirable attributes [1]. ITO is a ceramic, and is, therefore, brittle and prone to cracking. The abundance of indium in the earth's crust is low (0.05 ppm), and its cost is correspondingly high, reaching approximately US$700/kg in 2014 [2]. To solve these problems, various types of transparent electrodes based on nanoscale materials have been developed over the past twelve years [3, 4]. Recently, as an alternative to ITO, copper nanowires (CuNWs) have been studied extensively for use in fabricating transparent conductors.

Copper has extremely low resistivity, 1.7×10^{-8} Ω m at 293.15 K, higher than only silver and carbon graphene. Its price was US$5.22/kg in 2015, 100 times less expensive than silver and indium [5]. Many reported studies show remarkable performance of CuNWs thin films. Over the past decade, there are two general synthesis methods for CuNWs: ethylenediamine (EDA)-mediated synthesis and alkylamine-mediated synthesis. The alkylamine-mediated synthesis is usually carried out under neutral or moderately basic conditions at a high temperature, under a high pressure; this synthesis requires at least 10–12 h [6–9]. The CuNWs produced by this method have diameters of 30–100 nm and lengths up to several millimeters. On the other hand, EDA-mediated syntheses are several-fold faster, requiring less than an hour, and can be performed under atmospheric pressure [10–14]. However, the aspect ratios of CuNWs produced by this method are typically lower

than those produced by alkylamine-based synthesis. In 2014, Ye et al. developed a rapid method that required only 30 min and afforded high aspect ratio CuNWs with an average L/D of 1860 [10]. While the yield of CuNWs produced by the EDA-mediated method is low, about 12%, Ye et al. developed a novel two-pots method to improve the production of CuNWs by using cuprous oxide seeds, resulting in a yield of 55% [11]. However, this method is complicated and requires a longer time.

In this paper, we present an edited EDA-mediated synthesis that is simple, rapid, and gives high yields of high aspect ratio Cu NWs. Generally, EDA-mediated method uses sodium hydroxide as a pH adjusting element (NaOH) and keeps the reaction at high temperature from 60 to 80 °C. Herein, we used potassium hydroxide (KOH) as base source and maintained reaction temperature at room temperature. Moreover, the as-synthesized Cu NWs was coated onto soda lime glasses to make transparent electrodes.

Experimental

Synthetic procedures

To synthesize Cu NWs, KOH (15 M, 20 mL), $CuCl_2$ (0.1 M, 1 mL), and EDA (2.25 mmol), were placed in a 50 mL flask and stirred at 650 rpm for 2 min while retaining the mixture temperature at 60 °C. N_2H_4 (35 wt%, 15 μL) was then gently added dropwise, and the mixture was stirred for an additional 1 min. Then the mixture was left to cool down at room temperature (RT, 25 °C) until a reddish cake was formed. Next, the cake was transferred to a 50 mL tube and washed with 10 mL aqueous solution consisting of 1 wt% polyvinylpryrrolidone (PVP, MW 30,000) and 1 wt% diethylhydroxylamine (DEHA). The Cu NWs were washed with the above solution 3 times by centrifuge at 2000 rpm, 5 min and stored in the same solution.

Mass measuring

Furthermore, due to the increase in the thickness of the Cu NWs cake in the preliminary experiments, a short experiment was carried out to measure the mass of the synthesized Cu NWs. To increase the measurement accuracy, all experiments were conducted with double the volume used in the previous experiments. After the cake was formed, it was washed 3 times with deionized (DI) water. HCl solution (10 mL, 6%) was then added to remove unwanted organic impurities and copper (II) oxide. The mixture was centrifuged at 4000 rpm for 10 min to remove residual HCl, copper chloride, and unwanted chemicals. The mixture was washed once again with DI water. Following this, the mixture was filtered under vacuum to obtain pure Cu NWs on a polytetrafluoroethylene (PTFE) membrane with a pore size of 0.2 μm. The difference in the mass of the membrane before and after filtration indicated the mass of Cu NWs produced by this synthesis.

The yield of synthesis process was calculated by the following express:

$$\text{Yield} = \frac{\text{Mass of as-synthesized CuNWs}}{\text{Mass of used Cu}} \times 100\%.$$

Copper nanowires electrodes preparation

Generally, the Cu NWs electrodes preparation, which was carried out in this study, is similar with the one of Steward et al. [15].

First, nitrocellulose, also known as cellulose nitrate, was synthesized. 10 mL mixture of H_2SO_4 98% and HNO_3 70% (ratio 7:3) was prepared in ice bath. Then 0.5 mg cotton was added to this mixture. To make sure all the cotton was fully wet, the mixture was stirred hardly at 700 rpm for 30 min at room temperature. After being fished out, the cotton was washed thoroughly in sodium bicarbonate solution 2 times and in DI water 3 times to neutralize the pH of cotton. Then the cotton was left in air for 6 h to dry completely. Next, to prepare the nitrocellulose-based ink, 0.24 mg nitrocellulose was dissolved in 11.76 mg acetone with hardly stirring for 15 min. Then 12 g ethanol, 2 g ethyl acetate, 4 g pentyl acetate, 4 g isopropanol, and 6.8 g toluene were added, respectively. The nitrocellulose-based ink was formed by stirring this mixture for 10 min.

Before mixing with the nitrocellulose-based ink, the stored Cu NWs sample needed to be purified from PVP and DEHA. This cleaning step was carried out by washing the sample 3 times with DI water and 2 times with ethanol. Then, Cu NWs were transferred to an aliquot (1 mL) and washed with nitrocellulose ink once. After pouring off the ink wash supernatant, 0.5 mL nitrocellulose-based ink was added to the Cu NWs to make the final coating solution. Next, 30 mL of this solution was pipetted in a small line across the top of the glass substrate (7 cm × 2.5 cm). Right after that, a Meyer rod was rapidly and manually drawn down the substrate to equally disperse the copper nanowires coating solution.

Due to being covered by nitrocellulose-based ink, the Cu NWs film requires a post-treatment step to be conductive. First, the coated film was dried in air for 10 min at 80 °C, then was left to cool down to room temperature. Next, it was plunged gently in glacial acetic acid for 2 s, dried under air, and kept in oven at 80 °C for 45 s. After four cycles of this procedure, the film was cooled down to

room temperature and then dipped in glacial acetic acid and dried under air twice more without additional oven drying. Finally, the post-treated Cu NWs film was stored under N_2 gas to avoid oxidation.

Results and discussion

Effect of KOH and cooling to room temperature (25 °C)

First, it took only 15 min to form a reddish cake of Cu NWs by using our method. From the author's knowledge, no synthesis method of Cu NWs is quicker than ours. Normally, the alkylamine-mediated syntheses usually require from 6 h to several days [6–9]; while among ethylenediamine-mediated synthesis methods, the shortest time to form a Cu NWs cake is 30 min [10–14]. Until now, the mechanism underlying EDA-mediated synthesis of Cu NWs process has remained unclear; however, it is confirmed in previous studies that there are three vital elements necessary to form CuNWs. First, at least one pH adjusting species to form a first solution to make a suitable environment is required. Second, the reducing agent is used to reduce copper (II) ion into copper particle. Third, the capping agent which has skilled abilities to prevent copper atoms from freely growing, and help them to grow uniformly also plays key role in Cu NWs synthesis. A concentrated NaOH solution was commonly used to prevent the formation of copper hydroxide precipitates from copper ions [13]. However, once the concentration of NaOH reached 15 M, it became more difficult to achieve complete dissolution, and solid NaOH pieces remaining within the solution cover the copper atom, prevent them from contacting with the capping agent EDA, and finally caused the production of copper particles only [12]. On the other hand, KOH flakes easily dissolved in water to form a 15 M solution; hence, it is more suitable for raising the pH of the solution and enhancing the reduction of copper by hydrazine. This may be the reason for the outstanding result observed when using KOH instead of NaOH: a significant reduction in reaction time.

Next, the as-synthesized Cu NWs were analyzed using a scanning electron microscope (SEM, Hitachi S-4800). As shown in Fig. 1 The average diameter and length of CuNWs were about 71.43 nm and 46.71 μm, respectively. Interestingly, if the reaction temperature maintained at 60 °C, the reaction time was only 10 min but the obtained Cu NWs had an average diameter of 85.14 nm and an average length of 33.39 μm. It has been shown in previous studies that heat is required to accelerate the formation of nanowires [16]. However, excessive heat has been shown to be the cause of formation of relatively short and thick Cu NWs [14]. Therefore, after the reaction mixture was heated at 60 °C for only a short time (3 min), it was cooled to RT with the expectation of obtaining longer and thinner Cu NWs. And the data produced in this study showed a notable increase in both the length and diameter of the Cu NWs when the reaction mixture was maintained at RT instead of 60 °C. Furthermore, when the mixture was cooled to room temperature, the total mass of the synthesized Cu NWs remarkably raised from 17.73 to 80.16%. This leads to the presumption that RT conditions enhance both the aspect ratio of CuNWs and the productivity. While other reported EDA-mediated synthesis methods require reaction temperature above 60 °C for longer than 30 min to attain the highest yield at 60%, this simple discovery will help in significantly reducing the cost of Cu NWs synthesis.

In addition, a sample of as-synthesized Cu NWs were prepared for X-ray diffraction analysis. X-ray diffraction (XRD) of Cu NWs sample was measured in the range of $2\theta = 20°–80°$ by step scanning on the Rigaku D/MAX-2500 diffractometer (Rigaku Co., JAPAN). As shown in Fig. 2, all recorded peaks in the XRD pattern match to the face centered cubic phase of copper and no impurities can be observed.

Characteristic of copper nanowires electrodes

To fabricate various transparent conducting electrodes of Cu NWs, 10 coating solutions with different concentrations of Cu NWs were prepared and then were coated onto glass substrates with a Meyer rod, as shown in Fig. 3. The optical transmittance of the electrode was measured using PowerWave HT Microplate Spectrophotometer of BioTek and the sheet resistance of electrode was measured using "four-point probe" method. The relationship between transmittance and sheet resistance of Cu NWs was established in Fig. 4. The transmittance and sheet resistance increase dramatically with the decrease of Cu NWs density. The as-synthesized Cu NWs exhibited excellent performance with high transmittance and low resistance. For instance, the Cu NWs films displayed sheet resistances of 15, 23.5, 27.5 Ω/sq at transmittance of 72, 81, 82.5% at $\lambda = 550$ nm, respectively. Compared with the Cu NWs electrodes which were fabricated with the same procedure by Stewart et al. [15], our Cu NWs electrode exhibited equivalent performance. Moreover, the performance of our films is similar or slightly better in comparison with other

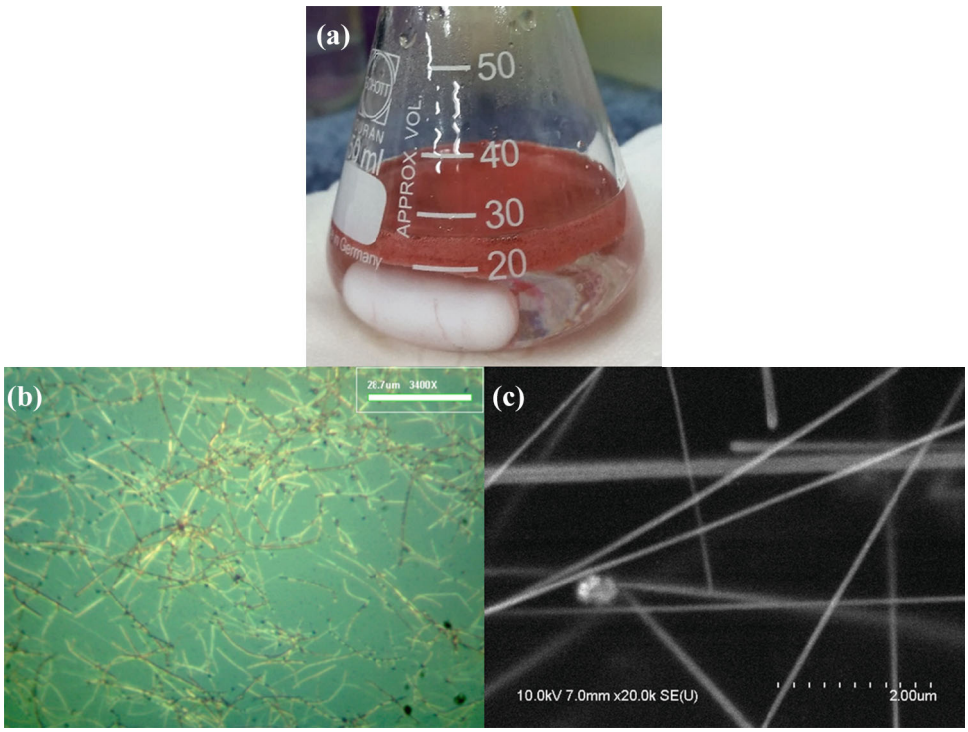

Fig. 1 **a** The reddish cake of Cu NWs, **b** video scope image of Cu NWs (scale 28.7 μm), **c** SEM image of Cu NWs

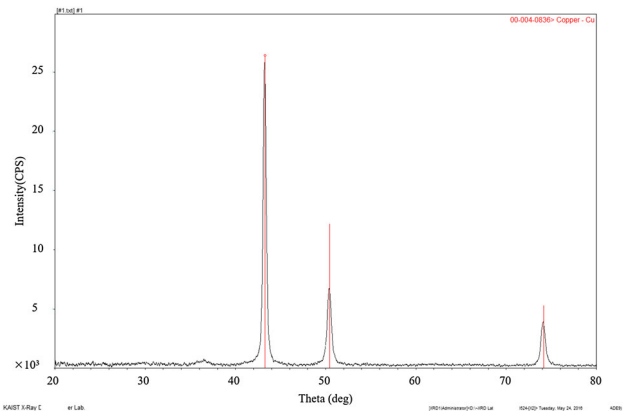

Fig. 2 XRD result of as-synthesized copper nanowires

Cu NWs films which also went through the acetic acid-treatment step [17, 18].

Conclusions

In this paper, an EDA-mediated synthesis has been developed to fabricate high aspect ratio Cu NWs (L/D ~650) within a very short time, at low cost. The yield of the Cu NWs produced by this method was increased outstandingly to 80.2%. Furthermore, we discovered that KOH could speed up the formation of Cu NWs to reduce synthesis time to 15 min; cooling the reaction to room temperature has a marked effect on the aspect ratio of the nanowires

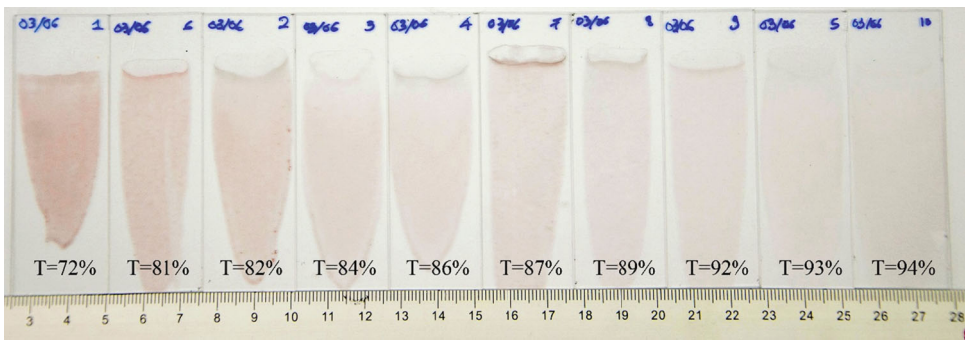

Fig. 3 Pictures of 10 samples with different concentration of CuNWs (from *left* to *right*: the concentration descends)

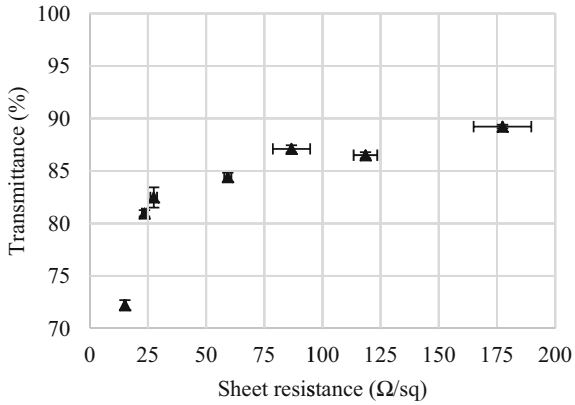

Fig. 4 Plot of transmittance ($\lambda = 550$ nm) vs. sheet resistance for films of Cu NWs

produced. In addition, the as-synthesized Cu NWs were used for the fabrication of transparent electrodes and these electrodes exhibited low sheet resistance and high transmittance.

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